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RESEARCH AND APPLICATIONS BRANCH

MID-YEAR PROGRESS REPORT

1989-90

R E S E A R C H A N D A P P L I C A T I O N S B R A N C H

MID-YEAR PROGRESS REPORT

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PREAMBLE

In keeping with a practice established some time ago, it is my pleasure to present to our clients, collaborators and colleagues this mid-year progress report about the activities of the Research and Applications Branch, National Water Research Institute, covering the period April 1 to September 30, 1989.

This document is intended to provide an overview of the various projects and activities underway in the Branch and communicate higlights of the results obtained. Readers interested in obtaining additional information or providing comments on any particular study are invited to contact the appropriate study leader or the Branch Director's Office.

John Lawrence
Director
Research and Applications Branch

LIST OF ACRONYMS

AED	Atomic Emission Detector
C&P	Conservation and Protection
CAP	Coupled Argon Plasma
CAPCO	Canadian Association of Pesticide Control Officials
CCIW	Canada Centre for Inland Waters
CEPA	Canadian Environmental Protection Act
CHCL	Clean and Hazardous Chemical Laboratory
CI	Chemical Ionization
CPPA	Canadian Pulp and Paper Association
CRM	Certified Reference Material
DNA	Deoxyribonucleic acid
DOE	Department of the Environment
DQAC	Dioxin Quality Assurance Committee
ECD	Electron Capture Detector
EI	Electron Impact
EP	Environmental Protection
EPA	Environmental Protection Agency
ESRF	Environmental Studies Research Fund
FIA	Flow Analysis Injection
FICP	Federal Interdepartmental Committee on Pesticides
FP	Federal-Provincial
FTB	Floating Tire Breakwater
GC/MS	Gas Chromatography/Mass Spectrometry
GLC	Gas Liquid Chromatography
GLERL	Great Lakes Environmental Research Laboratory
HPLC	High Pressure Liquid Chromatography
HRGC	High Resolution Gas Chromatography
IA	Immunoassay
IJC	International Joint Commission
IMD	Ion Mobility Detector
IRQC	Interregional Quality Control
IWD	Inland Waters Directorate
LC	Liquid Chromatography
LC/MS	Liquid Chromatography/Mass Spectrometry
LC_{50}	Lethal Concentration for 50% of test population
LRB	Lakes Research Branch
LRTAP	Long Range Transport of Atmospheric Pollutants
LSB (MOE)	Laboratory Services Branch (Ontario Ministry of the Environment)
LSE	Large Sample Extraction
MS/MS	Mass Spectrometry/Mass Spectrometry
NICI	Negative Ion Chemical Ionization
NWQL	National Water Quality Laboratory

List of acronyms (continued)

NWRI	National Water Research Institute
PAH	Polynuclear Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PCDD	Polychlorinated Dibenzo-p-dioxin
PCDF	Polychlorinated Dibenzofuran
PESTMYOP	Pesticide Multi-year Operational Plan
PFB	Pentafluorobenzyl
PID	Photoionization Detector
PPQ	Part per Quadrillion (10^{-15})
PPT	Part per Trillion (10^{-12})
PPWB	Prairie Provinces Water Board
QA	Quality Assurance
QC	Quality Control
RAB	Research and Applications Branch
RFA	Resin and Fatty Acids
RIA	Radioimmunoassay
RM	Reference Material
RRB	Rivers Research Branch
RSD	Research Support Division
SFC	Supercritical Fluid Chromatography
SFE	Supercritical Fluid Extraction
SWADE	Surface Wave Dynamics Experiment
SWAPP	Surface Wave Processes Program
TCDD	Tetrachlorodibenzo-p-dioxin
TCDF	Tetrachlorodibenzofuran
TDD	Tyramine Dioxin Derivative
TMA	Texel-Marsden-Arsloe
WAWSP	Wave and Wave Stress Prediction
WQB	Water Quality Branch
WRB	Water Resources Branch
WSC	Water Survey of Canada

RESEARCH AND APPLICATIONS BRANCH

J. Lawrence, Director

OVERVIEW

The Research and Applications Branch (RAB) is one of the three research branches of the National Water Research Institute (NWRI). The mission oriented research activities carried out by the Branch are grouped into three projects, namely the Analytical Chemistry Research Project, the Quality Assurance Project and the Hydraulics Studies Project. In the following pages of this report, a general overview of each project is provided as well as a progress report on each study currently under way.

The RAB research program focusses on specific priority needs identified by the various components of Environment Canada, particularly the Conservation and Protection Service. Major clients for the output of the Branch activities include other Branches within the Institute, National and Regional laboratories of the Water Quality Branch, the Water Resources Branch, and various agencies with responsibility in areas such as Federal/Provincial Water Quality Agreements, Long Range Transport of Atmospheric Pollutants and Great Lakes Water Quality Agreement.

The Branch is continuing to devote efforts in various ways to maintain and, where feasible, increase the level of technology transfer with the university and private industry sectors. The Branch offers a wide range of specialized equipment, services and facilities that can be used or accessed by external parties within full or partial cost recovery, in accordance with the Treasury Board guidelines.

I. ANALYTICAL CHEMISTRY RESEARCH PROJECT

ANALYTICAL CHEMISTRY RESEARCH

I. Sekerka, Project Chief

INTRODUCTION

The main objectives of the Analytical Chemistry Project of the Research and Applications Branch are: to develop new and improved analytical methods as well as screening and sampling procedures which are accurate, cost-effective, sensitive and unambiguous for the identification and quantification of contaminants in aquatic ecosystems; to play a lead role in documentation, validation and standardization of analytical methodologies to ensure accuracy and reliability of analytical data; to provide NWRI with sophisticated instrumentation and facilities; and to transfer developed methods and technologies to the national and regional laboratories of Conservation and Protection and a wide variety of other "clients".

HIGHLIGHTS

Operation of sophisticated instrumentation and facilities

A tribid mass spectrometer has been acquired jointly by NWRI and the National Water Quality Laboratory (NWQL). This instrument is versatile enough to be used by NWQL for routine analyses of organics and by NWRI for research activities on mass spectrometry.

One study is focused on the operation of the Clean and Hazardous Chemicals Laboratory where facilities are available for carrying out analytical work on highly toxic contaminants at ultra-trace levels. The laboratory offers maximum protection to workers and minimizes cross-contamination of samples. Currently, priority samples are being analyzed for dioxins and furans.

Detection of toxic and mutagenic effects at sub-cellular level

A study is underway to develop techniques capable of detecting sub-cellular level evidence of effects linked to the toxic, carcinogenic or mutagenic properties of pollutants. Laboratory techniques are being developed to routinely determine and characterize compositional and physiological changes in genetic material and associated protein substances. These techniques are intended to assist in the screening, categorization and control of environmental contaminants by providing valuable information on their potential to cause adverse effects.

Development of analytical methods

Liquid chromatography (LC) with multi-detection capability offers a great potential for analysis of a wide range of compounds differing from each other in terms of volatility or molecular weight. The high pressure/liquid chromatography multi-detection system is being used for developing improved methods for the analysis of polynuclear aromatic hydrocarbons. The analytical potential of the above system, in conjunction with pre-column and post-column derivatization, will be explored.

Research efforts are devoted to the optimization of operating conditions of gas-liquid chromatography (GLC) systems coupled with advanced computer techniques in order to systematically group unknown peaks in the chromatograms of environmental samples. Result files from the data-collecting computer can be transferred to powerful portable computers or, where appropriate, to larger computer systems for analysis and manipulation of the data.

Screening techniques are under development for the detection of trace organic contaminants. In previous years, a radioimmunoassay (RIA) for the detection of polychlorinated dibenzo-p-dioxins was developed. In that work problems were experienced with the labeled dioxin derivative (hapten) used in the RIA. An alternative hapten has been synthesized and is undergoing evaluation in the RIA technique using both polyclonal and monoclonal antibodies, with particular attention to the validation of the extraction and cleanup steps. As part of the study, an evaluation of two immunoassay methods for the detection of atrazine and related triazine herbicides in water will also be completed. An improved rapid extraction and cleanup procedure for use with these immunoassays will be developed and validated.

Research is being carried out for the development of an analytical method for the determination of the resin and fatty acids commonly found in pulp mill effluents. Existing methods lack the sensitivity required for many environmental samples. The formation, GC resolution, cleanup and analysis of the pentafluorobenzyl ester derivatives of the resin and fatty acids will be examined, along with the use of mass spectroscopy under negative ion chemical ionization as the analytical method.

Organic acids are relatively less known than inorganic acids, partly due to the fact that they readily disintegrate and, therefore, the analysts do not usually find them during analysis. Yet they are present in most samples and are an integral part of the various processes in the aquatic

environment. The application of liquid chromatographic methodology is being investigated for the determination of organic acids in environmental samples. Once the optimum operating conditions have been determined, the method will be applied to the analysis of pulp mill effluents.

Development of extraction, pre-concentration and injection techniques

The extraction and recovery of organic contaminants is a critical and often limiting step in analysis schemes used to identify and determine organic pollutants. In this context, research is continuing on various methodology aspects associated with the use of supercritical fluids for analytical extractions. The approach can provide a powerful alternative to traditional extraction techniques in that supercritical fluid extractions can be performed at low temperatures and usually no pre-concentration procedures are required, thus reducing the potential for loss of analytes and possible thermal degradation.

Large sample extraction technology, developed within the Analytical Chemistry Project, has become a routine pre-concentration method for the determination of "target compounds" at parts-per-trillion levels. The technology was accepted by the "Four Parties" administering the Niagara River Toxics Management Plan as the method to be used. The technology has been applied successfully in Great Lakes surveillance toxics monitoring. A study currently under way is devoted to the development of the large-sample extraction systems for use with a variety of environmental aqueous matrices and to integrate the pre-concentration technology with improved "cleanup" and analytical procedures.

The flow injection analytical system (FIA), developed by the Project, has been shown as capable of bringing effectiveness and economy in large scale environmental analytical work. FIA methods are now used on a routine basis for the determination of alkalinity, acidity and various ions. Research is being carried out on ways to optimize the system, with particular emphasis on robotization aspects for various steps of the methodology.

Study 84006: The Operation of the Mass Spectroscopy Laboratory

by *

H.B. Lee, K. Terry and R.J. Wilkinson

INTRODUCTION

Mass spectrometers are presently the most versatile and powerful tools in the analysis and confirmation of trace organics in environmental samples. Although many smaller quadrupole mass spectrometers are in use in laboratories located at the Canada Centre for Inland Waters (CCIW) for simple and routine applications, these units have low resolution and lack the flexibility of providing different ionisation techniques and different sample introduction and interface systems. In order to support analytical services and research activities of more demanding mass spectral requirements, a mass spectroscopy laboratory was set up and a VG Tribrid mass spectrometer was acquired, jointly with NWQL, on a lease-to-own basis.

RESULTS

The VG Tribrid is a medium resolution hybrid mass spectrometer characterized by the incorporation of three types of analyzers in the system. The instrument was chosen primarily because of its flexibility to accomodate the various research needs within NWRI as well as the requirements of NWQL for routine dioxin analysis. Although the instrument arrived in late 1988, it was not properly set up by the manufacturer until the end of August 1989, because of the lack of a workable software and a few hardware problems. During the installation period, samples were analyzed to confirm that factory specifications were met. For instance, an injection of 1 pg of tetrachlorodibenzo-p-dioxin (TCDD) present in an environmental sample produced under medium resolution (2000) a signal to noise (S/N) ratio of 10:1 using six ions. Because of hardware problems with the quadrupoles, MS/MS experiments on dioxins have not yet been completed. Analysis of pentafluorobenzyl (PFB) ester derivatives of resin and fatty acids was also performed on the tribrid under negative ion chemical ionization (NICI) conditions using methane as a reagent gas and the

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* In collaboration with J. Carron and A. Cassita (NWQL).

Study 84006 (continued)

results were fully satisfactory. The approach of alternating electron ionization (EI) and chemical ionization (CI) in the operation ofthe instrument for dioxin/furan analysis is being investigated. Information is being gathered to establish whether the instrument would be suitable for applications such as investigative GC/MS analysis of complicated sample extracts, automated operation, and thermo- or plasmaspray LC/MS analysis.

Study 84007: Electrokinetic and Enzymatic Detection of Subcellular Toxic and Mutagenic Effects

by

S.A.Daniels and F.I.Onuska

INTRODUCTION

The evaluation of pollutants in terms of their toxic, carcinogenic and mutagenic effects is largely confined to the determination of mortality, the occurrence of tumors, and of imperfections in offspring. It is appropriate then to look "below the surface" to determine what causes death, tumor formation, and deformed young. The development of laboratory techniques to routinely determine and characterize compositional and physiological changes in genetic and associated protein substances, would provide the capability to screen, categorize, and regulate environmental contaminants with a much greater appreciation for their potential detrimental effects.

To achieve these objectives, standard DNA preparations are selectively disrupted by specific enzymes to enable the laboratory detection and quantitation of resulting gene changes by electrokinetic protein differentiation procedures. Once these techniques have been perfected, they will be evaluated for the detection of specific contaminant-induced effects on DNA and other biomolecules. Should this evaluation give positive results, these techniques should be applicable to the assessment of effects caused by contaminants in aquatic organisms.

The goals of the research carried out in the current study are: (i) to establish a laboratory and the capability to effectively characterize low and high molecular weight proteinaceous material; (ii) to develop laboratory facilities for applying appropriate techniques to the characterization and analysis of nucleic acids; (iii) to evaluate the ability of these procedures to detect mutagenic phenomena.

Study 84007 (continued)

RESULTS

The laboratory is now adequately equipped and functional. Techniques of protein separation and analysis have been established. Good separations based on molecular weight have been achieved using preparations of myosin, phosphorylase (b), bovine serum albumin, ovalbumin, carbonic anhydrase, trypsin inhibitor, and lysozyme. Gradient and uniform SDS-polyacrylamide gels have been employed in these electrophoretic procedures. Southern electroblot gel-transfer techniques have also been established.

To accelerate the process of establishing the laboratory capability to analyze, characterize and manipulate nucleic genetic material, technology sharing arrangements have been put in place for collaboration between S. Daniels and Dr. Allan Bernstein of the Mount Sinai Research Institute. As a result, first hand experience has been obtained with current clinical investigative practices in the areas of DNA and nucleic acid isolation, gene analysis and sequencing as means of detecting and characterizing mutagenesis. Methods employed in gene splicing and cloning as well as the use of DNA probes in analysis and investigations were also explored.

The modification of some of these techniques for application to environmental investigation is currently underway as part of this study.

Densitometry software has been acquired and is currently being incorporated within the analytical system to assist in the acquisition, organization and analysis of data.

Publications

Daniels, S.A. Improving the elutriation technique for testing the bioavailability of contaminants in sediments. 1989. NWRI Contribution 89-94.

Study 84008: Development of Liquid Chromatographic Multi-Detection Technique Systems

by

B.K. Afghan and R.J. Wilkinson

INTRODUCTION

This new study has been initiated to explore the analytical potential of hyphenated liquid chromatography for the characterization, identification and determination of environmental pollutants at micro- and ultratrace levels. Until recently, liquid chromatography (LC) has been used extensively in biochemical and biomedical application where relatively polar compounds are analyzed in biological matrices. High pressure liquid chromatography (HPLC) incorporating multi-detection technology offers a great potential for the analysis of environmental samples. The method allows the separation of complex mixtures with constituents ranging from volatile to non-volatile and with molecular weights spanning over 3 to 4 orders of magnitude. The potential of HPLC is relatively greater for semi-polar and polar compounds because the parameters affecting the separation (the stationary and mobile phases) can be varied over a wide range of polarity and chemical functionality. In addition, the analytical measurements to obtain quantitative, multi-dimensional and fingerprinting information can be greatly improved by linking liquid chromatography to a wide range of detection techniques such as refractive index measurements, Fourier transform infrared spectroscopy, fluorescence, electrochemical techniques and mass spectrometry.

The objectives of this research project for the future are: (i) to automate and validate HPLC multi-detection system as part of the development of analytical methods for screening as well as measuring specific compounds at trace and ultra-trace levels; (ii) to explore the potential of pre- and post-column derivatization to improve selectivity and sensitivity for the detection of chemical and biochemical constituents in environmental samples, effluents and solid wastes.

Study 84008 (continued)

RESULTS

A number of HPLC systems are being set up for the analysis of substances such as PAH, carbamates and organo-sulfur compound. Each system will be linked to a different detection technique and operating conditions will be optimized to obtain maximum selectivity and sensitivity.

A literature search was carried out to review the current information available for over 100 different industrial chemicals and various pesticides. The literature search covered areas such as use, properties, occurrence and analytical methodologies with special reference to HPLC.

Preliminary performance verification of LC-MS was undertaken by analyzing selected candidate compounds deemed to be representative of the following classes of substances: organochlorine compounds, organo-phosphorus insecticides, carbamates, triazines, phenols, amines and PAHs.

Study 84011: Supercritical Fluid Extraction and Chromatography

by

F.I. Onuska and K. Terry

INTRODUCTION

The use of supercritical fluids for the extraction of organic substances and its application to environmental analysis are being investigated under this study since 1988-89. Recent results from studies on the extraction of polychlorinated biphenyls (PCBs) have demonstrated a wide range of possibilities for this extraction technique. The work currently underway will examine various aspects that need to be addressed in the development and evaluation of a SFE-GC system, namely design, construction, interface, detection systems and automation.

RESULTS

A simple method has been developed for the direct coupling of supercritical fluid extraction (SFE) with a high resolution gas chromatography (HRGC) equipped with and electron capture detection (ECD). SFE conditions have been investigated for the quantitation of PCBs in sediments in terms of mobile phase, entrainer, pressure, temperature and mass-flow through the extractor. The dynamic leaching and static steady-state extractions were compared. Extraction efficiencies of up to 100 percent in less than 15 minutes have been obtained. The extracted PCBs are quantitatively transferred into a fused silica open tubular pre-column accumulator. Determination of PCBs was tested on certified sediments from the NWRI and the results agreed well with certified values.

As part of this study, the feasibility of substituting a photoionization detector (PID) instead of the ion mobility detector (IMD) is being examined. Although the PID is still in its infancy as a fully characterized detection system for SFC, initial investigations of the detector have proved promising. This detector can be used with a variety of mobile phases and it has been successfully demonstrated in supercritical fluid chromatography (SFC) under pressure/density programming, with carbon dioxide, CO_2/methanol, ethylene or nitrous oxide used as the mobile phase.

Study 84011 (continued)

An attempt to design an interface for the SFE-quadrupole mass spectrometry has been initiated, but this work has fallen behind schedule due to delays in the machine shop work portion of the project.

Publications

Onuska, F.I. and K.A. Terry. 1989. Supercritical Fluid Extraction of PCBs in Tandem with HRGC in Environmental Analysis. J. High Resoln. Chromatogr., 12:527-531.

Onuska, F.I. and K.A. Terry. 1989. Identification and Quantitative Analysis of N-containing Polycyclic Aromatic Hydrocarbons in Sediments. J. High Resoln. Chromatogr., 12:362-367.

Onuska, F.I. and K.A. Terry. 1989. Quantitative HRGC and Mass Spectrometry of Toxaphene Residues in Fish Samples. J. Chromatogr., 471:161-171.

Mudroch, A., F.I. Onuska and L. Kalas. 1989. Distribution of PCBs in Water, Sediment and Biota of Two Harbours. Chemosphere, 18:2141-2154.

Presentations

Onuska, F.I. Supercritical Fluid Extraction as a Novel Analytical Tool in Environmental Samples Preparation. Presented at the 10th International Symposium on Capillary Chromatography, Riva del Garda, Italy, May 21-25, 1989.

Study 84012: Preconcentration for Ultra-trace Analysis

by

D.J. Anthony

INTRODUCTION

Several activities of Environment Canada's IWD require the identification and quantitation of toxic organic contaminants in water at "ultra-trace" (ppt, ppq) levels. These activities include background level monitoring, agreement monitoring (e.g.,. Niagara River Toxics Management Plan) and pathways studies. For many of the "target" organic contaminants of current concern as well as for compounds likely to be investigated in future broad spectrum analysis studies, conventional analytical techniques cannot provide the sensitivity required for accurate identification and quantitation. Research conducted in this study endeavours to provide practical contaminant preconcentration techniques whereby the contaminants in a sample may be concentrated to a level permitting unambiguous and accurate determination by conventional instrumental techniques (e.g., GC-MS, GC-ECD). Research is continuing on the development of the large sample solvent extraction (LSE) technology, with emphasis on determining the suitability of supercritical fluid extraction (SFE) as a preconcentration technique for the activities mentioned above.

The following objectives have been established for the study during FY 89/90: (i) to investigate the modifications required to carry out specialized large sample extractions, including aspects linked to the extraction process and the extraction apparatus; (ii) to further develop LSE technology to improve routine use in a variety of laboratory and field applications; (iii) to study the feasibility of solid phase adsorption/supercritical fluid desorption as a preconcentration system for organic contaminants determinations.

RESULTS

Samples from experiments in large sample solvent extraction of "special" matrices such as pulp and paper mill effluents and bog water (high humic/fulvic acids content) have been analyzed and the results are presently being evaluated. These results will indicate the suitability of present large sample extraction technology in processing such matrices and indicate possible improvements in the chemical/physical aspects of the method.

Study 84012 (continued)

The assembly of a prototype large sample extractor, with solvent recovery incorporated as a feature, is near completion. The apparatus will be tested under field conditions at the Niagara-on-the-Lake monitoring station during the remainder of this study period, through cooperation with staff of the WQB Great Lakes Surveillance Division.

A survey of recent research literature relating to the supercritical fluid extraction (SCFE) of environmental matrices has been completed. Relevant information was also gathered on documented cases where commercial SFE equipment has been tested as a preconcentration technique for the extraction of organic contaminants from aqueous matrices.

Presentations

Anthony, D.J. An Overview of Field Applications of Large Sample Extraction Technology. Presented at the NWRI-MOE Methods Development Seminar, CCIW, Burlington, Ontario, May 24-25, 1989.

STUDY 843013: Continuous Flow Analytical Systems Research

by

I. Sekerka and J.F. Lechner

INTRODUCTION

The research work carried out under this study is focussed on two general goals, namely to develop analytical methods as required by water quality assessment and to optimize the effectiveness and economy of environmental laboratories and environmental monitoring. The "Flow Injection Analysis (FIA) system" that has resulted form previous research activities under this study has been shown to meet the two goals stated above. FIA methods for Mg^{+2}, Ca^{+2}, Ba^{+2}, Na^{+}, B^{+3}, K^{+}, NH_4^{+}, NO_3^{-}, NO_2^{-}, PO_4^{-3}, CN^{-}, alkalinity and acidity are now used on a routine basis. In order to streamline certain aspects of FIA system such as increasing the rate of sample introduction into the system (up to 300 samples per hour), efforts have been devoted to the development of an automated robot system. In its final version, the robot system should handle entire strings of operations required for the analysis such as sample identification, sample delivery to the analyzer, operation of the analyzer, data collection, calculation of the results, statistical evaluation and storage of the data.

The following objectives have been established for the work carried out currently under this study: (i) examine the introduction of in-line systems into continuous flow automated analysis to improve the economy and efficiency of the preconcentration and digestion steps of the analytical procedure; (ii) a previously developed iso-thermal distillation system will be examined as part of the development an automated continuous flow method for the determination of ammonia; (iii) progress in the robotization of analytical chemistry procedures will continue with the validation of the reliability of the developed system under long-term routine analysis conditions.

Study 84013 (continued)

RESULTS

Research toward an improvement of the preconcentration and digestion steps of automated FIA systems is progressing. Results are collected from comparative tests of UV and Microwave digestion approaches.

The experimental part of the development of the method for ammonia has been completed. Results are being evaluated and a report is in preparation.

The robotic system has been installed for testing purposes within the operations of the National Water Quality Laboratory. When the system is used in conjunction with a FIA-CAP analysis system, good results have been obtained in determinations of the following ions: Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}, and B^{+3}.

Presentations

Sekerka, I. and J.F. Lechner. FIA Method for Boron Determination. Presented at the NWRI-MOE Methods Development Seminar, CCIW, Burlington, Ontario, May 24-25, 1989.

Sekerka, I. and J.F. Lechner. Automated Method for the Determination of Boron in Water by FIA with In-Line Preconcentration and Colorimetric Detection. Presented at the International Symposium on Detection in Liquid Chromatography and Flow Injection Analysis, Cordoba, Spain, September 1989.

Sekerka, I. and J.F. Lechner. Iso-thermal Distillation in Continuous Flow Analysis. Presented at the Third International Symposium on Kinetics in Analytical Chemistry, Dubrovnik, Yugoslavia, September 1989.

Study 84014: Broad Spectrum Analysis

by*

B. F. Scott

INTRODUCTION

The object of this study is to systematically group the peaks of non-target compounds in the chromatograms of environmental samples to obtain optimal information from the analysis of the samples. At present, in a chromatogram of any environmental sample, the target compounds contribute only a few peaks to the many detected. The focus of the study is to combine the optimization of gas-liquid chromatography with advanced computer techniques. Also it is necessary to investigate the utility of any new detectors that can be used on gas chromatographs which will provide additional information as to structural features of the non-target compounds or for "fingerprinting" a series of samples from the same area over time. Another aspect of the study is to facilitate the transfer of result files from one computing system to another where the files will be subjected to various chemometric techniques.

After successfully developing a method for PCB congener analysis by dual capillary gas chromatography operated with an electron capture detector (ECD), efforts were initiated to transfer result files to sophisticated portable computers. At this time, concern over the possible presence of contaminants in re-refined fuels resulted in a shift in the direction of this study. A number of the fuel samples collected in the Ontario Region were analyzed for PCB content at concentration levels down to the low ppb. Also, to conform to the intent of the Interim Order issued at the time of this incident, a new detector which can analyze organic sulphur and phosphorous compounds was evaluated and subsequently purchased for the analysis of collected fuel samples. This instrument has been installed in the National Water Quality Laboratory. The combination of improved computer capabilities resulting from the development of the PCB methodology with the latest development in detector technology such as the atomic emission detector (AED), will offer a unique analysis system to a variety of users.

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* In collaboration with A. Cassita, R. Sampson and J-G. Zakrevsky (NWQL).

Study 84014 (continued)

RESULTS

Fuel samples were analysed with the PCB methodology developed recently and published earlier this year. The main feature of this analytical method consists of the division of a single injection onto two capillary columns of differing polarity, with each column attached to a separate EC detector. Generally EC detectors are used to analyze halogenated organic molecules. Chromatograms of all fuel samples were very complex with many peaks identified as organo-chlorine compounds, including PCBs. Through various correlations of data obtained from the chromatograms, reliable information was assembled on the level of PCB contamination in the fuel samples analysed.

In relation to the Interim Order issued at the time of the tainted fuel incident, another requirement arose for the analysis of fuel samples for possible contamination of organic sulphur and phosphorous compounds. The coupling of an atomic emission detector (AED) recently introduced in the market place was evaluated and found to be appropriate for the requirement. The sensitivity of the detector varies, depending on the element, but generally the sensitivity is at least that of the flame ionization detector. Several of the fuel samples subjected to the congener specific PCB methodology were analyzed on the Cl and Br channels of the AED. This new detector system, on account of being element specific, shows promise to open new possibilities as part of the continuing work carried out under this study.

Since the acquisition of the AED, several aspects of the detector such as the reproducibility of the injector and analysing system and the linearity of response are the object of on going investigations. These studies have been carried out to a large extent in the course of analyses of sulfur- and phosphorous-containing pesticides normally done by the NWQL and analyses of various fuel samples. The preliminary results obtained from these studies are encouraging in terms of the performance of AED systems in broad spectrum analysis.

Publications

Scott, B.F., Cassista, A. and R.L. Hong-You. 1989. Analysis of Contaminated Fuels. NWRI Contribution 89-129.

Scott, B.F. and F.I. Onuska. 1989. Analysis for Polychlorinated Biphenyls by Dual Capillary Column Chromatography. J. Microcolumn Separations, 1: 119.

Study 84016: Operation of Clean and Hazardous Laboratory and Separation of Organic Substances

by

B.K. Afghan and R.J. Wilkinson

INTRODUCTION

Environmental monitoring for hazardous substances such as polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) at ultra-trace levels (ppt and ppq) has increased significantly. The current programs and regulations related to PCDDs and PCDFs are anticipated to maintain a steady growing demand for the services of the Clean and Hazardous Chemical Laboratory (CHCL). The work under this study will continue to provide the necessary analytical reference data as well as to improve methodologies for the analysis of various congeners and isomers of dioxins and furans in environmental and related matrices.

RESULTS

The draft version of an analytical protocol for the determination of PCDDs and PCDFs was prepared at the request of Environment Canada's Industrial Programs Branch. This protocol is proposed as a reference method in activities linked to the monitoring and control of PCDDs and PCDFs in pulp and paper media. The proposed method is under review within Environment Canada, Fisheries & Oceans Canada and the pulp and paper industry.

The following is an overview of the analytical work carried out during the reporting period. The operation and services of the Clean and Hazardous Materials Laboratory were interrupted for over three weeks in late March - early April for maintenance work in the facilities. Approximately sixty pulp mill sludge or sediment type samples have been analyzed as part of a Lakes Research Branch investigation of whether higher chlorinated dioxins and furans can be dechlorinated under specific conditions to produce the tetrachloro isomers 2,3,7,8-TCDD or 2,3,7,8-TCDF, respectively.

Study 84016 (continued)

Fifteen large volume aqueous effluent samples were analyzed as part of a Research and Applications Branch project to determine if the large volume sampler developed by Goulden & Anthony could be used to sample large volumes of pulp mill effluents for dioxin/furan analyses. Three check samples were analyzed for dioxins/furans and reported on under a Quality Assurance study run by the RAB-QA Project. At the request of the Water Quality Branch, six fish tissue samples were analyzed for dioxins/furans and the results reported to the originator of the request. Twelve sediment type samples collected under a pulp and paper mill effluent study were analyzed for dioxins and furans.

Study 84017: Screening Techniques for Toxic Substances

by

J.P. Sherry

INTRODUCTION

Conventional methods for the analysis of trace organic contaminants in environmental samples are generally time consuming and expensive. Often, many samples, eventually shown to be contaminant-free, must nevertheless be extracted and cleaned-up before being analyzed using GC or GC/MS. The inclusion of screening steps in analytical protocols would, by the elimination of contaminant-free samples from subsequent analysis, greatly reduce analytical costs. Samples that test positive using the screening assay would be confirmed and quantified using conventional methods. Of the available screening tests, immunoassays (IA) appear to offer the most promise. Based on the classical antigen-antibody reaction, IAs are relatively simple, powerful and adaptable to techniques for the rapid detection of trace levels of organic compounds. Most IAs cost about a few dollars per assay, although some commercially available kits can cost about $20 per sample. Current research interests in this area at NWRI include the development of radioimmunoassay (RIA) techniques for PCDDs, and the determination of their performance characteristics with a variety of environmental matrices. Eventually it is hoped to have a battery of screening tests for the detection of a range of environmental contaminants.

RESULTS

The synthesis of a tyramine dioxin derivative (TDD) was completed and reported on at the Dioxin 89 Conference. Mass spectrometric analysis of this compound was undertaken. Several variations of the chloramine-T driven labelling reaction were evaluated using the TDD. As a result, an improved molecule was designed and is currently being synthesized.

An evaluation of an effective and efficient extraction and clean-up method for use in the analysis of PCDDs by radioimmunoassay was completed and reported on at the Dioxin 89 Conference. This work included a comparison of the improved and existing extraction and clean-up procedures.

With the micro-plate version of the Immunosystems Assay, a detection limit of 12.5 ppt was achieved without

Study 84017 (continued)

difficulty. An excellent dose response was achieved between 12.5 and 50 ppt. A set of 15 environmental water samples was also analyzed. The samples were from a variety of locations and contained various levels of Atrazine. Good agreement was observed between the IA and GC results (correlation coefficient of 0.94). Further tests are planned with this system. The results of this study were provided to Immunosystems Inc., to assist them with product development.

A rapid sample preparation technique was developed for use in conjunction with the IA screening technique. It is planned to complete validation of this method, and to interface it with the screening assay as an ancillary project.

Publications

Sherry, J.P. 1989. A Comparison of the Abilities of 15 Media to Recover Viable Yeasts from Pond, River, and Lake Water. J. Microbiol. Methods, 10:39-46.

Presentations

Sherry, J.P. and H. Tse. An Effective and Efficient Extraction and Clean-up Method for the Analysis of PCDDs in Fish. Presented at the Ninth International Symposium on Chlorinated Dioxins and Related Compounds (ANA 32), Toronto, Ontario, September, 17-22, 1989.

Sherry, J.P., J.W. ApSimon, T.L. Collier and P.W. Albro. Further Development of a Radioimmunoassay for the Detection of PCDDs. Presented at the Ninth International Symposium on Chlorinated Dioxins and Related Compounds (ANA 48), Toronto, Ontario, September, 17-22, 1989.

Collier, T.L., J.W. ApSimon and J.P. Sherry. Development of an Improved Hapten for Use in the Radioimmunoassay of Dioxins. Presented at the Ninth International Symposium on Chlorinated Dioxins and Related Compounds (ANA 49), Toronto, Ontario, September, 17-22, 1989.

Study 84018: Identification and Determination of Toxic Organics in Pulp and Paper Industry Effluents

by

H.B. Lee and T.E. Peart

INTRODUCTION

Pulp and paper industry effluents are known to be highly toxic to fish and other aquatic organisms. Among the toxic components, resin acids and some unsaturated fatty acids were identified as the major contributors to the toxicity in pulpmill effluents. While these acids and chlorinated phenolic compounds also found in the effluents have similar 96 hr LC_{50} values, the levels of the acids are often higher than those of the phenolics. The existing analytical methodology for the determination of resin acids is not sensitive enough for the monitoring of such acids in the many final effluents discharged into the environment. Thus there is a need to develop a more sensitive method for the determination and confirmation of resin and fatty acids (RFA) in pulpmill effluents.

RESULTS

Pentafluorobenzyl (PFB) esters were used in the analysis of RFA since these derivatives are easily formed, stable and have strong sensitivity in electron capture detection (ECD) systems. Separation of the PFB esters of all commonly found RFA was achieved by using either a DB-5 or a DB-17 capillary column. RFA in effluents were extracted by methyl t-butyl ether, derivatized, and cleaned up on a silica gel column. Since the electron capturing PFB esters produce abundant and characteristic $(M-181)^-$ ions under negative ion chemical ionization (NICI) conditions, NICI mass spectrometry

Study 84018 (continued)

can be used in the confirmation as well as quantitation of RFA in effluents. Based on a 25 mL sample and a concentration factor of 10, the method detection limit for all acids was 1 µg/L. This method is being applied to the determination of RFA in Canadian pulpmill effluents.

Publications

Lee, H.B., T.E. Peart and J.M. Carron. 1989. Gas Chromatographic and Mass Spectrometric Determination of Some Resin and Fatty Acids in Pulpmill Effluents as Their Pentafluorobenzyl Ester Derivatives. NWRI Contribution 89-125.

Study 84019: Development of LC Methodology for Analysis of Environmental Samples

by

V. Cheam

INTRODUCTION

Organic acids are relatively unknown compared to inorganic acids, partly due to the fact that they readily disintegrate, and therefore the analysts do not usually find them during analysis. Yet they are present in most samples, and are an integral part of the various processes forming the living environment.

This study is focussed on the development of a liquid chromatography (LC) methodology for the analysis of organic acids in environmental samples. An evaluation of the Ion Exclusion Chromatography mode will be made first, followed by its comparison with Anion Chromatography modes. Individual precision and accuracy data as well as overall ruggedness will be obtained and assessed. It is intended to apply to the analysis of pulpmill effluents the mode that will be identified as the preferred one .

RESULTS

Three methods were set up to study the seventeen acids potentially present in precipitation samples. The methods were isocratic anion exchange chromatography, ion-exclusion chromatography, and gradient anion exchange chromatography. The results obtained so far on the resolution of the acids by the three methods show the superiority of the gradient mode in terms of number of acids resolved. However, the following points are noteworthy: (i) if only the more common organic acids (formic, acetic, propionic, butyric, lactic and glycolic) were of interest, the preferred method would be ion-exclusion chromatography, because it is more rugged and gives better peak resolution than the gradient mode; (ii) likewise, the isocratic anion exchange mode is preferred if only the more common inorganic acids (hydrofluoric, hydrochloric, sulfuric and nitric) were of interest; (iii) if data on both type of acids are required, both the ion-exclusion and the isocratic anion methods have to be used concurrently, whereas only one gradient method is needed; (iv) a comparison of individual performance characteristics and overall ruggedness needs to be considered before the final conclusion can be made.

Study 84019 (continued)

Publications

Cheam, V. 1989. Determination of Organic and Inorganic Acids in Precipitation Samples. NWRI Contribution 89-93.

Presentations

Cheam, V. "Simultaneous analysis of organic and inorganic acids in precipitations samples", presented at the 6th International Symposium on ion chromatography, Sils-Maria, Switzerland, April 9-12, 1989.

Cheam, V. "Organic and inorganic acids in rain samples", NWRI-MOE Methods Development seminar '89, CCIW, Burlington, Ontario, May 24-25, 1989.

II. QUALITY ASSURANCE

QUALITY ASSURANCE PROJECT

A.Y.S. Chau, Project Chief

INTRODUCTION

The mandate of the Quality Assurance (QA) Project is to heighten awareness with respect to the need for a coordinated quality assurance program and to contribute expertise as needed to ensure that analytical data generated for Environment Canada are of good comparable quality. The Project is essential for successful management and utilization of water resources and for research on water pollution, particularly in the areas of toxic chemicals and acid rain. The ability of Environment Canada to provide authoritative and reliable scientific advice on control and remediation strategies is crucially dependent on the availability of high quality scientific data.

Chemical and biological data are essential to all decisions made by government with respect to environmental assessment and pollution control. Biased measurements can lead to errors in assessment and in subsequent control actions. In addition, the expense of data collection and interpretation makes the cost of discarding questionable data very high; therefore, data must be compatible, reliable and suitable for the intended use. A comprehensive QA program is the essential first step in the gathering of reliable data for use in environmental assessments. As its long term goal, the QA Project strives to assist in the development of comprehensive quality assurance programs in all relevant sectors of the Department.

As the lead body responsible for quality assurance, the QA group:

(a) plans, coordinates, and implements quality assurance and control programs to ensure accuracy, comparability and reliability of analytical data;

(b) develops and prepares Certified Reference Materials [CRMs] (water, sediment and biota) and reference materials for use in quality assurance and analytical methods research and environmental assessment studies;

(c) provides a consultation service on QA to Environment Canada, other federal departments, provincial agencies, and international establishments.

Typical project activities include the design and conduct of various interlaboratory comparison studies as well the provision of support in the areas of methodology evaluation and sample preservation for departmentally sponsored projects that have an analytical data collection component.

The QA Project is also initiating an active marketing component in advertising its products and expertise. In this regard, the first phase of the marketing activity is to advertise more aggressively the CRMs developed and prepared by the QA group. Also as resources and time permit, papers on QA and CRMs are presented at scientific conferences and symposia. Three papers were presented to international conferences during this period.

HIGHLIGHTS

The following paragraphs highlight special projects and activities not addressed in study progress reports.

Dredging QA Program

Upon request of Public Works and EP Toronto Office, the QA Group was given $30K to revitalize the Dredging QA Program, particularly to assist the managers of the dredging projects to select commercial laboratories for analysis and assure the data quality.

Biomonitoring QA Guidelines

The QA Project has played a key role in the organization and chairing of a committee that has been given the mandate to develop a set of biomonitoring QA guidelines. The committee is made up of representatives of provincial and federal government agencies and private sector companies.

Technical Transfer and Consultation

The QA group provides a leading role on QA matters and acts as Chairman or appointed members of multi-agency national and international bodies such as the QA Committee of the Association of Official Analytical Chemists (AOAC), the Dioxin QA Committee of the DOE Dioxin Task Force, the Data Quality Work Group of the IJC and the Canadian Advisory Committee on QA Management of the International Standards Organization (ISO). In addition, expert advice on QA/QC matters is provided on a regular basis in response to request originating from within and outside the Department.

Extensive advice and consultation were provided to the Ocean Dumping Advisory Committee of the Environment Canada C&P-Pacific and Yukon Region, on matters pertaining to Quality Assurance in dioxin/furan analysis. QA project staff collaborated in the development of a detailed QA protocol that should be applied to dioxin/furan analysis data as part of the review of proposals for the ocean disposal of marine sediments.

Study 84021: Organic Quality Assurance

by

Y.D. Stokker and A.S.Y. Chau

INTRODUCTION

The provision of interlaboratory Quality Assurance studies for various organic parameters is a valuable and very necessary service for any laboratory involved in environmental management, monitoring and surveillance, or research. Under this study, the Organic QA project designs, conducts, and provides interpretation of interlaboratory quality control (QC) studies in support of the Canadian Association of Pesticide Control Officials (CAPCO), the Federal Interdepartmental Committee on Pesticides (FICP), the Federal/Provincial Quality Assurance Program, and the National Dioxin QA Program. As well special studies are carried out as part of the National QA Program. Each participating laboratory receives a summary of all interlaboratory data from which peer appraisals can be made. Precision and accuracy data can be determined for each laboratory when blind duplicates and CRMs are included among the samples distributed.

The effectiveness of interlaboratory Quality Assurance studies, intralaboratory Quality Control, and analytical methods research is strongly dependent on the availability and use of reference materials (RMs) and certified reference materials (CRMs). These may be analytical standards, either neat or in solution, sample extracts, or natural substrates such as samples of water, sediment or biota. They must be stable, well characterized, and homogeneously subdivided into identical aliquots. Their matrices should be identical, or at least very similar, to those of the field program materials in order to eliminate or greatly reduce the matrix effect between reference and test samples. The target value for each parameter must be well established and supported by sufficient valid documentation. Each RM and CRM should be periodically monitored in order to ensure the stability of all parameters over time.

Effective Quality Assurance programs are built around two main groups of activities: (i) the design, execution and interpretation of interlaboratory QC studies; and (ii) the development and certification of standard reference and certified reference materials. The major goals pursued this year under the Organic QA Program are as follows:

Study 84021 (continued)

(1) to prepare reference samples in ampules for organic compounds;
(2) to complete two National Dioxin Interlaboratory QA studies;
(3) to initiate, design and conduct two interlaboratory QA studies for other organic QA programs (FICP/CAPCO, Fed/Prov);
(4) to screen sediment CRMs for selected organic parameters;
(5) communications and marketing of the QA product and expertise.

RESULTS

A reference sediment extract was prepared by extraction with acetone of 2.0 kg of freeze-dried sediment from Lakes Erie and St. Clair. The extracts were filtered, combined and concentrated until each 1.0 mL of extract represented 2.0 g of the original freeze-dried material. Previous work had revealed the presence in this material of approximately 100 ng/mL PCBs, 10-1000 ng/mL PAHs and 1-50 ng/mL chlorobenzenes. The extract was fortified with 1-5 μg/mL each of trifluralin, triallate, atrazine, alachlor and metolachlor. "Standard" solutions were also prepared to match the concentration levels in the sediment extract. In total, more than 1400 ampules containing these five neutral herbicides of interest were sealed. Homogeneity and stability tests were begun immediately on these reference extracts and are continuing. The preparation of these reference materials in ampules was supported this year by the PESTMYOP Program.

Ampules of standard solutions were also prepared for several Aroclor blends, polynuclear aromatic hydrocarbons and for fenitrothion. These analytical reference standards in ampules were provided to many federal and provincial government laboratories as well as to laboratories in the private sector in support of their research and monitoring programs and for in-house quality control check samples.

The National Dioxin Interlaboratory QC Study No. 1 on the analysis of dioxins and furans in sediments involved 17 laboratories, of which only eleven provided results. Four freeze-dried sediment samples, including two naturally-contaminated reference materials, were sent to each laboratory who had requested to participate in this new

Study 84021 (continued)

program. Each laboratory was asked to analyze for 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD), 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) and total tetra-, penta-, hexa-, hepta- and octachlorinated congener groups for both dioxins and furans. For the two sediments spiked with known amounts of 2,3,7,8-TCDD and 2,3,7,8-TCDF, the interlaboratory means and medians agreed well with the fortification levels. For these two isomers and for many of the congener group totals, there were some laboratories who displayed severe bias and/or had some extreme outliers. In general, however, the results appeared to indicate that several laboratories have the capability of providing sensitive and accurate analyses for dioxins and furans.

In a study being conducted under the auspices of CAPCO, (formerly the FICP National Check Samples Program), 26 laboratories across Canada have received sets of ampules containing five neutral herbicides in analytical standard solutions and in sediment extracts. This QC study is being conducted as part of the PESTMYOP study on sediment reference extracts in ampules.

Three special QA round-robin studies have also been initiated this year in response to special requests. The first study was linked to the tainted fuel incident of May 1989 when a large number of fuel samples were analysed for PCBs in various government laboratories. Following a special request by DOE Senior Management, the entire staff of the QA Project collaborated in the design and conduct of a round-robin study to assess the quality and reliability of the analysis data produced by the participating laboratories.

Another special interlaboratory QC study was conducted in response to a request by the Province of New Brunswick through the Groundwater Contaminants Group of the National Water Research Institute. This study, entitled National Interlaboratory QC Study No. 38 on the Analysis of Polynuclear Aromatic Hydrocarbons in Drinking Water, was undertaken to evaluate the capabilities of Canadian laboratories to analyze for a number of PAHs suspected of contaminating the municipal wells of Newcastle, New Brunswick. This round-robin study demonstrated that, although several laboratories are capable of performing sensitive analyses for PAHs, there remains some doubt as to their ability to accurately measure for certain PAHs, and in particular for benzo[a]pyrene, at the level of the drinking water guidelines.

Study 84021 (continued)

The third special organic interlaboratory QC study was requested by Environment Canada staff in the Atlantic Region. This study was undertaken to discover and assess the source of large differences in fenitrothion results being produced by two DOE laboratories. The round-robin study established that the data generated by the two laboratories were relatively comparable and that both analysts were capable of performing sensitive analyses for fenitrothion at each of the levels requested in this study. However, while the results indicated that there was no significant problem in the analysis of fenitrothion by either of the two participants, one of the laboratories was biased slightly low, thereby indicating a possible error in its in-house standard.

Approximately 2500 kg of Lake Ontario sediment was collected in June for development into a new lake sediment certified reference material. It is anticipated that his material will become certified for a wide range of organic and inorganic pollutants that will complement the range of existing RMs and CRMs produced by the QA group over the past ten years. Currently, arrangements are being made for funding and scheduling of the freeze-drying and sample processing of this sediment into its final bottled product.

Finally, as part of the QA team's marketing strategies for quality assurance and its products, the brochure advertising NWRI's Certified Reference Materials has been distributed at several conferences, symposia, trade fairs and external QA meetings. These brochures will continue to be widely distributed to laboratories involved in all fields of environmental studies, from applied and investigative research to routine monitoring and surveillance.

Publications

Stokker, Yvonne D. Preliminary Report on National Interlaboratory QC Study No. 38: The Analysis of Polynuclear Aromatic Hydrocarbons in Drinking Water. August 1989.

Stokker, Yvonne D. Preliminary PESTMYOP Report on the Preparation and Stability of Sediment Reference Extracts in Ampules. May 1989.

Study 84021 (continued)

Aspila, K.I., A.S.Y. Chau, Yvonne D. Stokker and W.C. Li. External Quality Assurance Study on PCBs in Gasoline. May 1989.

Stokker, Yvonne D. Preliminary Report on Special Organic Interlaboratory Study: The Analysis of Fenitrothion. September 1989.

Stokker, Yvonne D. and A.S.Y. Chau. Preliminary Report on National Dioxin Interlaboratory QC Study No. 1: The Analysis of Dioxins and Furans in Sediment. September 1989.

Study 84022: WQB, PPWB and Federal/Provincial Quality Assurance Programs

by

H. Alkema

INTRODUCTION

Quality Control Studies were initiated in the early 70's under request from the Water Quality Branch (WQB) as part of the ongoing interregional quality control program (IRQC). Presently, some 40 parameters in four water samples are sent out bimonthly to five regional WQB laboratories. Evaluation results for each bimonthly study are communicated quickly to participating, usually within weeks after receipt of the data. Six QA reports are prepared each year.

For the Prairie Provinces Water Board (PPWB), a QA program was initiated in 1982 as an ongoing program because there was "a need to improve the compatibility of federal and provincial water quality data being collected in interprovincial and international streams in Western Canada". At present, three provincial laboratories (Alberta, Saskatchewan and Manitoba) and two WQB laboratories participate to the program. The IRQC QA program was expanded and modified to meet the PPWB objectives of assessing long term data comparability and to enhance in-house quality control programs in these provincial and federal laboratories.

In the latter part of this decade, under several Federal/Provincial WQ agreements, five more laboratories were integrated with the IRQC-PPWB program. In the past year, with the privatization of the British Columbia Environmental laboratory, two private sector laboratories from that province have joined the Federal/Provincial program. At this time, a total of 19 laboratories are involved the Federal/Provincial and PPWB programs.

The laboratory results obtained under these programs are tested in absolute terms with the use of certified reference waters. Generally, the laboratories report their results in a timely manner and take corrective action when results are identified as anomalous.

Study 84022 (continued)

RESULTS

The QA/QC studies conducted under the programs described above have resulted in the preparation and distribution of 7 preliminary data evaluations and 6 final reports. A contract was arranged with the B.C. Ministry of Environment for the monthly delivery of audit samples to verify performance.

Special initiatives are underway toward improving the work carried out in this study. For instance, an extensive computer program for automated data evaluation and a major parameter dictionary revision has been developed and are being tested. Also, two reference waters were prepared for application over the long term in the FP/PPWB QA programs.

Study 84023: LRTAP Interlaboratory Quality Control Studies

by

K.I. Aspila, N. Arafat and A.S.Y. Chau

INTRODUCTION

The Federal-Provincial Long Range Transport of Atmospheric Pollutants (LRTAP) programs involve approximately 60 different laboratories that generate data on soft surface waters and precipitation samples. Many millions of dollars are invested in the laboratory production and use of these data. If these data are to be merged or used to define trends or acidic impacts, then these data must be unbiased and precise. This project helps define data quality, assists laboratories in taking corrective action and provides assistance to network managers who plan to merge data bases.

Studies for this project include ten soft natural waters that are distributed normally to between 50 and 60 laboratories. Analyses are requested for about 20 constituents. Results are analyzed for measurement bias using the nonparametric approach of Youden. Individual results that deviate significantly from interlaboratory medians are flagged either high or low. Studies are normally completed about eight weeks after distribution. Each laboratory is then provided a laboratory specific appraisal indicating its performance. Corrective action is suggested when performance is poor.

RESULTS

Since the start of the project in 1982, twenty studies have been completed. In 1989-90, three new studies have been planned, on major ions, nutrients and minerals, respectively. At the end of September, Study No. L21 had been completed, Study No. L22 was in progress, and Study No. L23 was scheduled for distribution in December.

The external QA studies program continues to demonstrate that laboratories can improve their performance when they participate frequently in an effective peer group audit program (the round-robins) and have a management attuned to Quality Management, Quality Assurance and Quality Control concepts. Improvements are induced by the collective efforts of analysts, managers, active input by users of data, and frequent studies using a powerful design and interpretive technique (Youden's nonparametric technique).

Study 84023 (continued)

Data assessment procedures are now heavily automated and utilize the mainframe Cyber computer to analyze the AQC data base (System 2000 format). Two new procedure programs, one for creating precision functions and another for providing valuable data on charge balance and conductance ratios have been developed to further assist in defining laboratory performance.

Precision functions illustrating how the interlaboratory standard deviations varies as a function of concentration have now been prepared. These functions provide valuable information to set the criteria required to correctly flag individual results that deviate significantly from target values.

To reduce cost and labor, a manual has been prepared to describe how QA data files can be created and transmitted by phone modem to the NWRI Cyber computer. When implemented in 1990, the electronic transfer will reduce labor costs significantly.

Seven 200 litre volumes of highly characterized audit waters were developed, prepared and delivered a US private sector company working under contract for the U.S. EPA. These soft water samples will be used to evaluate the performance of U.S. laboratories generating analytical data under the American acid rain program.

Study 84024: IJC Quality Control Studies

by

K.I. Aspila and A.S.Y. Chau

INTRODUCTION

Agencies that support the Canada-U.S. Great Lakes Water Quality Agreement routinely generate data on many environmental substrates. These analytical data are made available to the institutions of the International Joint Commission (IJC). To assist the users of this data and to help laboratories in creating high quality data, the Data Quality Work Group organizes interlaboratory studies.

Studies are evaluated by the nonparametric techniques of Youden and Wilcoxan. These techniques provide powerful methods to discern laboratory measurement bias. Individual results that deviate significantly from interlaboratory medians are also flagged high or low.

RESULTS

Under Study No. 62, the data obtained from the analyses of sewage effluent samples for total phosphorus have been received from participating laboratories. The study has been completed with the preparation of the final version of the reports to the laboratories.

Ampules required for Study No. 59 have been partially prepared. Study No. 59 and the sediment study No. 55 (Organics in Sediments) have been rescheduled.

Study 84025: External QA for the Eulerian Model Field Study

by

K.I. Aspila and J. Lee

INTRODUCTION

The governments of Canada, the United States of America and the Province of Ontario as well as the Electric Power Research Institute in America are continuing the collection of daily rainwater samples in their respective precipitation networks, under a project initiated in 1988. Chemical analysis data from these four networks will be merged and the Eulerian model for atmospheric transport will be evaluated.

To assist managers of the Eulerian Model Field Study Program, the QA group in the Research and Applications Branch has arranged to provide monthly interlaboratory performance evaluation studies. Participants in these studies include the four primary laboratories in the Eulerian program as well as several other laboratories (four or five). Each month these laboratories are provided ten precipitations samples for analysis of 14 specific constituents. Results are appraised for bias by the nonparametric method of Youden. Individual results that deviate significantly from interlaboratory medians are flagged high or low.

RESULTS

The interlaboratory studies were implemented in July 1988 and studies have continued since on a monthly basis. Laboratory specific appraisals were mailed to each laboratory within four weeks of completing each study. Results of each study have been entered into a SYS2K data base management system for future retrieval and use.

The performance of the four primary laboratories is considered quite good and the operational management team has indicated great satisfaction about the ability of the QA program to demonstrate that the participating laboratories can produce comparable data.

Study 84025 (continued)

The project included the preparation of low level (near detection limit) audit samples for daily analysis by each laboratory. This special study originally carried out in the spring of 1989 has been requested again for the winter of 1989.

Precision functions that illustrate how interlaboratory standard deviation varies as a function of concentration have been established. These relationships provide clear evidence to readjust the criteria to flag individual results that deviate from target values.

Study 84026: QA for the Canadian National Pulp Mill Dioxin Monitoring Program

by

A.S.Y. Chau

INTRODUCTION

At the time when the concept of a National Pulp Mill Dioxin Sampling Program was being developed by the Canadian Pulp and Paper Association (CPPA), Environment Canada, upon request from the Association, accepted the responsibility to organize the QA/QC aspects of the program on a cost-recovery basis. As a result, the QA Project Chief was asked to assist the Environment Canada Dioxin Task Force by constituting and chairing a QA Committee to support the CPPA's dioxin sampling program.

The Dioxin QA Committee (DQAC) was formed in September 1988 and has taken on as its main role the provision of advice to the CPPA and the DOE Dioxin Task Force on the adequacy of procedures adopted to collect, prepare, ship and analyze samples for dioxin and furan determinations (including recommended modifications if required) and on the acceptability of individual analytical results.

RESULTS

A detailed QA protocol was developed and finalized by the DQAC as working document specifically intended for the CPPA Monitoring Program. Since it is the only detailed document of its kind available at this time, the protocol has also been adopted within the DOE sediment monitoring program and the Ocean Dumping Program of EP (Pacific & Yukon Region).

Fourteen set of analytical data and chromatograms obtained from work on pulp, effluent and sludge samples were extensively reviewed by the DQAC members to ensure that the QA protocol is followed and the data are of suitable quality.

Study 84027: CEPA QA

by

A.S.Y. Chau, W. Li, Y. Stokker

INTRODUCTION

The successful implementation of various aspects of the Canadian Environmnetal Protection Act (CEPA) is critically dependent on the availability of reliable scientific data. These data are essential to all decisions made by the government with respect to environment assessment, pollution control and enforcement of legislation. In this context, the QA Project has initiated a new study to provide timely assistance on QA/QC matters to operational programs focussed on the implementation of CEPA, particularly those dealing with enforcement and compliance activities.

RESULTS

Interlaboratory Study for Dioxins and Furans

An interlaboratory study was designed and conducted for dioxins and furans in sediments. Some 220 invitations were sent out and close to 20 laboratories provided data. The results are being evaluated.

Sediment Reference Materials for Dioxins and Furans

In efforts to prepare reference materials for use in dioxin and furan analysis, investigations are continuing to identify a suitable source of contaminated sediments. A suitable site in Western Canada has not yet been found due to insufficient levels of dioxins or inappropriate matrix (such as too much pulp or oily materials for effective homogenization). As an alternative source, the large quantity of Lake Ontario sediments collected for the purpose of preparing reference materials contaminated with organic compounds will be screened for dioxins.

Special QC Check Samples for Dioxins and Furans

In support to the national monitoring project for "Dioxins and Furans in Bottom Sediment from the Vicinity of the 47 Canadian Pulp & Paper Mills Using Chlorine Bleaching", a set of quality control samples were prepared to monitor contract laboratories during the analytical contracts.

Study 84027 (continued)

Advice and Consultation

Extensive advice on QA and laboratory performance was given in support of the following programs: Ocean Dumping Program for Dioxin (Western & Pacific Region), Bottom Sediment Dioxin Monitoring Program (C&P, Headquarters), 3 B.C. Mill Dioxin Emergency Analysis (EP Headquarters).

III. HYDRAULICS STUDIES

HYDRAULICS STUDIES PROJECT

M.G. Skafel, Project Chief

INTRODUCTION

Fluid dynamics and the interactions of water with air, sediments, shores, and man-made structures are fundamental to many of the issues being addressed in the environment. The staff of the Hydraulics Studies Project address selected topics in wave mechanics, coastal, and fluvial engineering to provide new knowledge for use by water resource managers and engineers in Environment Canada and elsewhere. Special attention is given to understanding hydraulic processes that could lead to structural failure with serious environmental consequences.

The research program in wave mechanics creates new knowledge for the determination of accurate parameters related to fluxes of mass, momentum, energy and heat across the air/water interface. This work has direct consequences in understanding toxic gas transfer, diffusion of pollutants, wave prediction, lake circulation, seasonal thermocline development, weather forecasting and climatic change.

The coastal engineering program is focussed on advancing the understanding of wave mechanics and sediment transport in the coastal zone, such as the resuspension of cohesive sediment, prediction techniques to develop wave climate models for sediment resuspension studies, shoreline evolution, and wave-structure interaction.

The fluvial engineering study is directed at improved understanding of fluid mechanics, sediment transport in rivers, the development of new and improved techniques for monitoring river processes, and flow-structure interaction with special emphasis on cases where structural failure could lead to serious environmental consequences. Emphasis is placed on providing information for operational branches in Environment Canada. Results are often applicable to issues in other departments and to other water resources managers.

The Hydraulics Studies Project operates the Hydraulics and Sedimentology Laboratories and provides technical support to Institute scientists and engineers using these facilities. The Project also encompasses the National Calibration Service, charged with current meter repair and calibration, primarily for the Water Survey of Canada.

A lead role is taken by Project staff in technology transfer to other government departments, universities, and the private sector. The facilities of the laboratory, when not committed to Institute activities, are actively marketed so that these other agencies have the opportunity to use our facilities as a resource in their activities. The client projects undertaken are primarily in the realms of fluvial and coastal engineering, and the calibration of current meters.

Study 84031: The Surface Wave Dynamics Experiment (SWADE)

by

M.A. Donelan

INTRODUCTION

The following objectives have been set for the work carried out under this study: (i)to understand the dynamics of the evolution of the wave field in the open ocean; and (ii) to determine the effect of waves on air-sea transfer of momentum, heat and mass.

RESULTS

In the first half of this year the planning of the SWADE study has progressed to the point of the development of a firm experimental plan involving 13 buoys, five aircraft and 1 airship. The buoys will be deployed for six months starting at the end of September, 1990. As part of the planning of the study, a meeting was held in Burlington in August, 1989 for discussions among the various individuals involved in the project.

The design and prototype construction of the measuring and recording systems for the wave and flux measuring buoys in SWADE have been completed. The prototype was tested in the Gulf of Mexico, in the vicinity of a wave measuring system on an oil production platform. The comparative analysis of the data obtained from the tests is being done by M. François Anctil, a Ph.D. student from Laval University.

A scientific paper by R.A. Weller, M.A. Donelan and M.G. Briscoe, is in preparation on the scientific plans for SWADE and a related experiment called SWAPP.

Study 84032: Fluvial Engineering

by*

P. Engel

INTRODUCTION

The fluvial engineering study is directed at improved understanding of fluid mechanics, sediment transport in rivers, the development of new and improved techniques for monitoring river processes and flow-structure interaction with special emphasis on cases where structural failure could lead to serious environmental consequences. A significant portion of the work is directed at the provision of information to operational branches in Environment Canada. The results of the work are often applicable to issues in other government agencies and are relevant in the area of water resources management.

The work in this study is divided into three categories: branch research, joint research and cost recovery research. Branch research consists of studies conducted as part of the long term research plan of the Research and Applications Branch (RAB). Joint research studies that are consistent with long term RAB research plan are conducted jointly with government (federal, provincial, or municipal) agencies or the private sector through cost sharing agreements. Cost recovery studies are of a short term nature, site or product specific and are funded totally by the client within the Treasury Board guidelines.

RESULTS

Support to Water Resources Branch

Acoustic Flow Meters

The work on the development of an acoustic flow meter by the Water Survey of Canada (WSC) is continuing. The final draft report on the tests conducted on the Stork Flow Meter,

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* In collaboration with B.G. Krishnappan and Y.L. Lau (NWRI-RRB); M.O. Spitzer (WRB-Calgary); I. McLaurin, K. Wiebe and P. Zrymiak (WRB-Ottawa); B. Tassone (WRB-Vancouver).

Study 84032 (continued)

designed in Holland, has been completed. The report deals with the properties of the flow meter, an error analysis and hydrodynamic aspects of testing acoustic flow meters in a towing tank. The report is being reviewed by WSC.

Vertical Velocity Profiling

Work on a method to measure the mean velocity for flows with irregular vertical velocity profiles is continuing. The preliminary tests in the two meter flume have been completed and the data are being analyzed. The method will make it possible to measure flows in river cross-sections where standard methods do not apply.

Discharge Measurements under Ice

Work is continuing on a long term study with WSC to establish quality control criteria for discharge measurements in rivers with solid ice cover. The first phase, dealing with the development of a new type of calibration equation for current meters based on physical principles, has been completed. A computer program capable of generating a least squares calibration equation for Price type current meters has been completed. A draft report for review by WSC has been prepared. Work is continuing on the evaluation of different current meter suspensions for flow measurements under ice cover.

Experimental Program to Measure Flow Under Ice Cover

Work was carried out on the development of a comprehensive research program on measurements of flows under ice cover. Using principles of fluvial hydraulics and information from the literature, criteria were established for the selection of a suitable river cross-section where experimental measurement programs can be conducted. A draft report has been prepared for the Committee of Measurement of Flow Under Ice and the document is under review by WSC staff.

Study 84032 (continued)

Measurement of Suspended Sediment

Work is continuing on the development of a comprehensive strategy for the calibration of suspended sediment samplers used nationally by WSC. Work is proceeding on the implementation of the short term research program to set up the required quality control standards for the operational sampler calibrations. Work on the fabrication of a small facility for the evaluation and quality control testing of sediment sampler nozzles is nearly completed. A preliminary test plan for the short term research program has been submitted to WSC.

RAB Research

Vortices at Pump Intakes

Work was continued on the inception of air entraining vortices at multiple pump intakes. This work is being done to develop the required expertise for the modeling of pump intake structures for cost recovery projects. A draft report has been prepared and is presently being revised.

Cost Recovery Research

Dam Break Surges

A memorandum of understanding was prepared for Shawinigan Engineering Limited for an experimental investigation of the effects of unsteady flow on an stream bed subject to erosion as a result of a dam failure. After considerable consultation, the client decided not to proceed with the study as the minimum cost estimate for the study exceeded the client's budget.

Gibson Lake Power House Physical Model

A detailed proposal was submitted to Sandwell Swan Wooster, Consulting Engineers, on the design and construction of a physical model to conduct tests on the approach flow conditions for the design of a new hydroelectric low head power house at Gibson Lake, near Thorold, Ontario. After considerable consultations, the client did not need to proceed with the model study because the initial requirement for

Study 84032 (continued)

modeling as specified under the Ontario Hydro Commission's procedures was eventually waived.

Testing of Acoustic Flow Meters

A proposal consisting of a suggested test program and cost estimates for the testing of acoustic flow meters was submitted to Ramsay Lake Industrial Meters Ltd. Acceptance and finalization of the proposal is still pending.

Publications

Fast, E.J., P. Engel and K. Wiebe. 1989. Preliminary Laboratory and Field Evaluation of the AFFRA Acoustic Flow Meter. Water Resources Branch Internal Report. April 1989.

Engel, P., Y.L. Lau and M. Spitzer. 1989. Effects of Bed Level Fluctuations on Discharge Measurement in Alluvial Streams. NWRI Contribution 89-88.

Engel, P. and P. Zrymiak. 1989. Development of a Calibration Strategy for Suspended Sediment Samplers - Phase I, NWRI Contribution 89-121.

Presentations

Engel, P., Y.L. Lau and M. Spitzer. Effects of Bed level Fluctuations on Discharge Measurement in Alluvial Streams. Presented at the 9th Canadian Hydrotechnical Conference of the Canadian Society for Civil Engineering, St. John's, Newfoundland, June 8-10, 1989.

Study 84033: Coastal Engineering

by *

M.G. Skafel, C.T. Bishop, M.A. Donelan and J. Doering

Introduction

The objectives of this study are to develop techniques and models for wave prediction, shoreline evolution, wave interactions with the bottom such as resuspension of sediments, and wave-structure interaction.

Results

Shoaling Waves

The analysis of the field data in terms of the joint probability density function of heights and periods of shoaling waves is complete. The first laboratory runs, using a beach of slope of 1:40 in the wind-wave flume, are about to begin. Twelve wave staffs spaced 4 m apart and two run-up gauges are installed on the beach. An acoustic flow meter has been ordered and it will be used to examine flow under the breaking waves. Conditions in the flume have been chosen to model those of the field data, and preliminary results show good qualitative agreement.

One-dimensional Wave Hindcasting

The comparison study of four one-dimensional wave hindcasting techniques is nearing completion. The main emphasis of the work recently has been to compare the direction estimating capabilities of the models with field data from Lake Erie, Lake St. Clair, and the Gulf of St. Lawrence. Significant differences have been found, and are being examined.

Two-dimensional Wave Prediction Model

As part of a comparison of wave climate models, a two-dimensional model developed by NWRI's Donelan has been

* In collaboration with J.P. Coakley (NWRI-LRB).

Study 84033 (continued)

investigated. Differences were observed between predictions of NWRI's version of the model WAWSP and a version modified at the Great Lakes Environmental Research Laboratory (GLERL). This led to a detailed 'debugging' analysis by J. Hodson (RSD). This investigation is ongoing and is expected to be completed by the end of November 1989. Comparison runs with measured data and with one-dimensional models will then be undertaken.

Submarine Pipelines

Wave forces on submarine pipelines in trenches were studied in the laboratory. The trench configuration is the same as proposed for use in the Beaufort Sea, where trenches are required to place the pipelines below the draft of ice floe keels. It was found that the forces were similar to those reported in the literature for pipes on flat beds at the same total water depth.

Great Lakes Water Level Variations

The rejection in 1988 by the Journal of Great Lakes Research of a manuscript submitted by Bishop has prompted further research and more development of the ideas and has resulted in a thorough revision of the manuscript. In late 1988, a paper was published by others in the Cdn. J. Earth Sci. which purports to show a climate-induced oscillation in the level of Lake Ontario over the last 3300 years, with an amplitude of about 1 m and a period of several hundred years. Bishop's research indicates that the climate-induced variations in mean annual levels of the modern Great Lakes have probably not exceeded those on record since measurements began in 1815. A paper discussing this data was submitted by Bishop and Coakley (LRB) and has been published.

The revised manuscript on "Historical Variation of Water Levels in Lakes Erie and Michigan-Huron" is nearing completion and will be resubmitted to the Journal of Great Lakes Research.

A paper titled "Some Effects of Changes in Water Levels on Great Lakes Archaeology" is in preparation. It will be finalized after the J. Great Lakes Res. paper has been resubmitted. In this paper, natural and man-made variations in lake levels are reviewed. Interpretation of archaeological findings at coastal sites around the Great Lakes can be

Study 84033 (continued)

influenced strongly by changes in relative land-water elevations over time; several archaeological case studies are examined to demonstrate this.

Goderich Harbour Environmental Monitoring

A monitoring program was undertaken for Transport Canada, starting in 1984, to determine changes in water depths at Goderich Harbour which may have been caused by a rubblemound breakwater constructed in 1984-85. Results of the hydrographic survey conducted in 1988 were examined. These results, combined with those from 1984,1985 and 1986, indicated a general lowering of the lake bottom in the survey area, even at water depths of 10 m where negligible changes were anticipated. Consequently, C. Bishop and P. Zrymiak (WSC) held discussions with officials of Domtar Ltd. concerning the lowering (subsidence) of the bottom of Lake Huron in the vicinity of the company's salt mine. It now appears that subsidence of 30 to 50 cm due to mining activity in the survey area has occurred since 1984. Preliminary results and implications for Transport Canada have been discussed at two meetings held at the offices of Public Works Canada in North York. A final report is in preparation.

Miscellaneous

At the request of Public Works Canada, Ontario Region, C. Bishop undertook a brief cost recovery study to review reports concerning the design wave for a rubblemound breakwater at Bronte Outer Harbour. In particular, wave shoaling techniques from linear and TMA theories were compared. A letter report was sent to Public Works.

C. Bishop responded to a number of requests for information concerning floating tire breakwaters (FTB's). A marina operator near Picton, Ontario has expressed an interest in building FTB's commercially. Technology transfer to the individual through provision of reports and advice is ongoing. Public Works Canada is investigating the feasibility of using an FTB to provide wave protection at the CCIW offshore breakwater.

Study 84033 (continued)

Publications

Skafel, M.G., and C.T. Bishop. 1989. Flow Visualization Around a Pipeline in a Trench. NWRI RAB Technical Note: RAB TN-89-06.

Skafel, M.G., and C.T. Bishop. 1989. Wave Forces on a Pipeline in a Trench. NWRI Contribution No. 89-122.

Bishop, C.T. and J.P. Coakley. 1989. Stratigraphy of the Sixteen Mile Creek Lagoon, and its Implications for Lake Ontario Water Levels: Discussion. Can. J. Earth Sci. 26: 1074-1076.

Bishop, C.T. and M.A. Donelan. 1989. Wave Prediction Models. in: Applications in Coastal Modeling, V.C. Lakhan and A.S. Trenhaile (editors), Elsevier Science Publishers B.V., Amsterdam, 75-105.

Study 84034: Wave Mechanics

by

M.A. Donelan

INTRODUCTION

The objectives of this study are to discover or develop theories and/or models to describe and predict the interaction of wind and water, including surface waves; fluxes of mass and energy; turbulence; orbital velocity beneath breaking waves.

RESULTS

The analysis of Lake St. Clair data was approached from a new point of view: the fetch dependence was examined on a case-by-case basis rather than the conventional similarity analysis in which all cases are lumped together in non-dimensional form. It was found that there were systematic differences in the fetch dependence, however, the cause of these differences did not seem to be related to any observable physical parameters such as stability and wave age. The data set was small since attention was restricted to those cases for which the wind was offshore +10°. A closer look at the directional properties of the Lake St. Clair waves is being carried out to allow us to broaden the data base of fetch-limited cases to include those at larger angles (+40°) to the shore normal using wave fetch rather than wind fetch. A concerted attack on this problem is planned in the 2nd half of this fiscal year.

A large part of the effort in this study was devoted to the writing of a review paper on "Air Sea Interaction" for The Sea, Volume 9. The review will be published in the next few months.

Engineers have long been troubled with the difficulty of estimating orbital velocities near the surface of wind-generated seas. The literature contains at least six semi-theoretical approaches, none of which is generally regarded as satisfactory; the simple ones failing in accuracy, the more sophisticated in having excessive computational requirements. In collaboration with François Anctil (a Ph.D. student at Laval University) another method has been developed that is both simple and accurate. The method has been compared to existing methods and is currently being tested against actual data obtained using an acoustic current meter on a

Study 84034 (continued)

wave-follower on the research tower in Lake Ontario during an earlier (1987) component of this study.

The directional spectrum analysis is in progress and yielding several interesting results. The work is being done by M. Donelan (NWRI), I. Tsanis (McMaster University) and K. Kahma (Finnish Marine Research Institute). A paper has been published and three more are in preparation.

The crucial work on the separation of waves and turbulence has now been successfully tested and production analysis of the data is about to begin. The work is being done by W. Drennan (post doctoral fellow). A contract has been let with Dr. Gene Terray (Woods Hole Oceanic Institute, USA) to complete over the next few months the analysis of the acoustic current meter data at the same time as we complete the analysis of the drag sphere data.

Presentations

Tsanis, I. and M. Donelan, 1989. Wave Directional Spectra in Mixed Seas. 2nd ESRF International Workshop on Wave Hindcasting and Forecasting, Vancouver, April 1989.

Study 84035: Transfer of Toxic Gases

by

M.A. Donelan

INTRODUCTION

The objective of this study is to establish the dependence of the transfer of toxic gases at the air-water interface on the parameters of the interface.

RESULTS

Initial tests were designed to establish the characteristics of the new gas transfer flume. The flume meets or exceeds all its specifications having maximum centreline wind speeds of 24 m/s and 10.5 m/s in the circulating and vented configurations, respectively. The current speed can be varied between 0 and 60 m/s. The three profiling stations are in place and are capable of automatic profiling at steps of 1/40 mm. Chemical sampling systems are also in place and are undergoing tests.

A series of experiments to establish the mass transfer rate of organochlorine insecticides was conducted at various wind speeds. The gas chromatograph analysis of the samples is being conducted and will be completed in about a month. The corresponding physical experiments --- stress, heat flux, evaporation and wave characteristics --- will be conducted over the next month also. A paper under preparation and based on the work of N. Merzi, a post-doctoral fellow associated with the project, will provide a description of an air-tight recirculating gas transfer flume and cover the experimental program designed to study the mass flux of high molecular weight organic solutes at the air-water interface.

Study 84036: National Calibration Service

by

B. Taylor, D. Fekyt, C. Bil and B. Near

INTRODUCTION

This study encompasses the NWRI's commitment to calibrate and repair all flow meters owned and used by the Water Survey of Canada (Water Resources Branch, Environment Canada). This work is organized and conducted through the National Calibration Service. In addition to the services provided to Water Survey of Canada, calibration and instrument repair services are made available to outside clients on a cost recovery basis.

RESULTS

To date, 417 calibrations and 221 current meter repairs have been actioned on request from Water Survey Offices throughout the country or from external clients such as universities, provincial or federal government agencies, hydro utilities, private firms and a USA government agency. These requests have resulted in revenues of $12K for the first half of 1989/90, an amount significantly higher in comparison with the same period in 1988/89.

Funds have been requested as part of the main estimates for 1990/91 to cover major overhaul work of the tow carriage tank system. In order to ensure accuracy of the system, traceable to national standards, the carriage is calibrated every 6 months. The overhead monorail hoist for handling heavy components to and from the carriage has been upgraded to improve efficiency and safety of operations.

Study 84037: Hydraulics and Sedimentology Laboratory Operations

by

B. Taylor and Technical Services Staff

INTRODUCTION

Under this study, specialized technical staff as well as fully operational laboratories and equipment are provided in support of hydraulics and geotechnical research projects and related activities.

RESULTS

The human resources of the Technical Services Section were fully utilized to assist NWRI mission research as well as cost recovery projects (see Study 84038). Technical staff have provided hydraulics lab and field support to several projects in all three research branches of NWRI. Staff were assigned to studies on a task by task basis and records of time utilization were maintained. All costs related to individual studies were assumed by the respective projects.

The Sedimentology Lab staff are operating and maintaining the large common-user freeze drying equipment and conducting size analysis on sediments upon requests originating from within CCIW or from research staff at the Bedford Institute of Oceanography and the Centre St-Laurent. During the report period, 767 sediment samples have been analyzed and resulted in the preparation of 21 separate technical data reports. Settling tube development has now been completed and evaluation tests are currently under way.

Study 84038: Applied Research and Engineering

by

C.T. Bishop and the Scientific, Engineering and Technical Staff
of
Research and Applications Branch and Rivers Research Branch

INTRODUCTION

This is the umbrella study for all third party revenue jobs in the Project. In addition, administration and technical support is provided to third party revenue jobs in the Hydraulics Laboratory led by Study Leaders in Rivers Research Branch.

RESULTS

The following list summarizes the cost recovery activities carried out in the first half of fiscal year 1989/90. Funds generated to date total $49,000.

Client	Project	Revenue ($000)	Status
Various	national calibration	12.0	in progress
Gore and Storrie	manhole section calib.	7.5	complete
Public Works Can.	Bronte Harbour study	3.0	complete
Mr. D. Campbell	snowmobile ski tests	1.1	complete
Hayward Gordon	observation tank rental	1.2	complete
USEPA	cold room rental	21.0	in progress
National Defence	tower rental to DREO	3.2	in progress

Quotations are under preparation for two jobs that could generate approximately $30-40k. It has been a disappointing year so far in the area of third party projects in that other proposals for work totalling a value of over $125K were developed, but failed to materialize for various reasons.

Study 84039: Hydraulics Lab Public Relations and Third Party Revenue

by

C.T. Bishop, M.G. Skafel, W.B. Taylor and P. Engel

INTRODUCTION

The following objectives are pursued under this study: to increase awareness in Canada and the U.S. Great Lakes region of the NWRI Hydraulics Lab capabilities and its availability for third party work; to improve means of accommodating and conducting third party work; and to increase third party revenue to the Lab.

RESULTS

Issue no. 2 of the Hydraulics Lab Newsletter was distributed on schedule at the end of April. The inserts for the English version of the Hydraulics Lab brochure have been revised and printed. Work on the inserts for the French version is nearing completion. A 1.2 m long scale model of a Parshall flume is being constructed for the Globe 90 display; it will also be useful for Open House and other special tours of the Lab. Input was provided to assist in the preparation of the "Technology Transfer and Marketing Business Plan" which dealt with the creation of a Technology Transfer Section (TTS) within RAB. Amongst other duties, the TTS would be responsible for the utilization of the marketable capacity of the Hydraulics Lab. Significant advances in the second and third study objectives outlined above are waiting for a management decision on whether or not the TTS is approved. Numerous tours of the Hydraulics Lab were provided during this 6-month period to potential clients and visiting scientists. Notable among these were groups from the International Association for Hydraulic Research (IAHR) XXIII Congress, the IAHR Instrumentation Workshop for Hydraulics Laboratories, and the Flow Intrumentation Workshop of the Water & Wastewater Instrumentation Testing Association.